Short communication

Hydrogen production by water electrolysis using tetra-alkyl-ammonium-sulfonic acid ionic liquid electrolytes

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HIGHLIGHTS

- An improved performance of water electrolysis as measured by HER is observed with TEA−PS·BF₄.
- The novel electrolysis process operates with high efficiencies and high current densities.
- Hydrogen production increases with increasing temperature.
- This process decreases the activation energy for water electrolysis.

ARTICLE INFO

ABSTRACT

Triethylammonium−propanesulfonic acid tetrafluoroborate (TEA−PS·BF₄) is used as an electrolyte in the water electrolysis. The electrolysis of water with this ionic conductor produces high current densities with high efficiencies, even at room temperatures. A system using TEA−PS·BF₄ in an electrochemical cell with platinum electrodes has current densities (i) up to 1.77 A cm^{-2} and efficiencies between 93 and 99% in temperatures ranging from 25 °C to 80 °C.

The activation energy observed with TEA−PS·BF₄ is ca. 9.3 kJ mol^{-1}, a low value that can be explained by the facilitation of proton transport in the organised aqueous ionic liquid media.

The unexpectedly high efficiency of this system is discussed by taking into account the high conductivities associated with the Brönsted and Lewis acidity characteristics associated with these ionic conductive materials.

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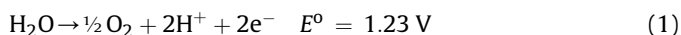
1. Introduction

Global sustainability depends on the balance of multiple factors, including the sources of energy and the production of environmental pollution [1]. Hydrogen, an energy source with high potential for improved energy storage capacity, has generated increasing interest as an environmentally clean technology [2,3].

Hydrogen used in industrial applications is currently produced by catalytic reforming reactions [4–7]. Various other methods of hydrogen production have been developed, including the water electrolysis. Interest in these other processes is limited, mainly due to economic reasons [8]. The most important factors in an evaluation of novel hydrogen production technologies are the cost and the availability of processing energy, a factor that is dependent on geopolitical conditions and varies in different countries around the world.

The half reactions occurring on the anode and cathode of electrolysis can be written in the following ways:

Anode (+):

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \quad E^o = 1.23\ V \tag{1}$$

Cathode (−):

$$2H^+ + 2e^- \rightarrow H_2 \quad E^o = 0.00\ V \tag{2}$$

The overall chemical reaction of the water electrolysis can be written as:

Overall reaction:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + H_2 \quad E^o = 1.23\ V \tag{3}$$

The availability of clean hydrogen produced from water electrolysis has an enormous impact on the choice of the fuel cell

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technology used to produce energy. The historical use of noble metals, such as palladium, for fuel cell electrodes is no longer necessary to resist the contaminants present in the hydrogen synthesised by reforming reactions. The expense of these types of metals can change the context in which this technology is important and viable.

With a combination of high conductivity and stability, ionic liquids (ILs) have been successfully used as electrolytes for water electrolysis and in other applications [9–13]. The availability of electrolytes that are able to perform water electrolysis with high efficiencies and high current densities has been thought of as the limiting factor in the economical industrial use of electrolysis, representing a non-negligible contribution in the development and implementation of a hydrogen economy [14,15].

Imidazolium based ILs have been used in the direct efficient electrolysis of water at room temperature using low concentrations of 1-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF$_4$) IL [14,16].

Even with favourable reaction stability characteristics, a major limitation in the development of technology using IL is the expense and the extensive time required for their synthesis.

In this work, new types of ILs are described that demonstrate both Brönsted and Lewis acidity characteristics [17]. These ILs are easily prepared from inexpensive reagents using simple procedures with short reaction times. One characteristic compound, 3-triethylammonium−propanesulfonic acid tetrafluoroborate (TEA−PS·BF$_4$), demonstrates advantageous abilities as an electrolyte in water electrolysis.

2. Experimental

The 3-triethylammonium−propanesulfonic acid tetrafluoroborate (TEA−PS·BF$_4$) is prepared by a reaction of 3-triethylammonium−propanesultonate (TEA−PS) with tetrafluoroborate acid (HBF$_4$).

2.1. Preparation of TEA−PS and TEA−PS·BF$_4$

The TEA−PS is prepared using procedures available in the literature [18]. In a typical reaction, 51.38 g of 1,3-propanesultone (Aldrich) and 42.46 g of triethylamine (Vetec) are mixed with 20 mL of ethyl acetate [19]. The reaction is stirred at 50 °C for 2 h and filtered, producing a white solid. The precipitate is washed with three aliquots of 10 mL of ethyl acetate and dried at 100 °C for 2 h, producing 3-triethylammonium−propanesultonate (TEA−PS) as a white powder [18] in a 61% yield. [^{1}H NMR (300 MHz, DMSO, ppm): δ 1.18 (t, 3H), 1.89 (m, 2H), 3.21 (m, 2H), 3.42 (m, 2H)].

The TEA−PS·BF$_4$ is prepared by reacting 56.78 g of TEA−PS dissolved in 4.6 mL of water and 31.5 mL of tetrafluoroboric acid (Riedel-de-Haën) at room temperature. After 2 h at 90 °C, the water is removed under reduced pressure, producing 75.98 g of 3-triethylammonium−propanesulfonic acid tetrafluoroborate (TEA−PS·BF$_4$) as a white viscous liquid in a 96% yield. [^{1}H NMR (300 MHz, DMSO, ppm): δ 1.17 (t, 3H), 1.88 (m, 2H), 3.22 (m, 2H), 3.32 (m, 2H), 4.23 (s, 1H). ^{13}C NMR (75 MHz, DMSO, ppm): δ 7.00, 17.78, 47.35, 51.97, 54.88].

2.2. Analytical procedures

Vibrational spectra (FTIR) were obtained using a Shimadzu FT-IR spectrometer Model RT-21 Prestige (KBr pellets). Nuclear Magnetic Resonance (NMR) spectra were obtained using a Varian VNMRs 300 using deuterated dimethyl sulfoxide (DMSO) as a solvent and tetramethylsilane (TMS) as the internal standard. The conductivity (σ) of the solutions was measured using a Hach

sension 7 conductivity meter. The pH values are determined using a pHmeter Digimed DM-22.

2.3. Electrolysis

The water electrolysis experiments are performed in a 100 mL *Hoffmann* cell [20] with platinum wires as the reference, working and counter electrodes. The working electrode area is 0.23 cm^2. The concentrations of the electrolyte used in the cell varied in the range from 0.1 to 0.7 M, and the temperature is controlled by a thermostatic bath in the range from 25 °C to 80 °C.

The system efficiency is calculated as the faradaic efficiency (η), defined as the ratio between the volume of hydrogen produced ($V_{H_2}^R$) in the cathode compartment during the electrochemical hydrogen evolution reaction (HER) and the ideal volume of hydrogen that should have been produced ($V_{H_2}^T$) if the measured charge had been completely used in the water electrolysis process:

$$\eta\% = \frac{V_{H_2}^R}{V_{H_2}^T} \times 100 \qquad (4)$$

where $V_{H_2}^R$ is the volume of hydrogen measured experimentally using the *Hoffmann* cell, and $V_{H_2}^T$ is the theoretical volume of hydrogen calculated by the following equation:

$$V_{H_2}^T = \frac{Q}{2F} \frac{RT}{P} \qquad (5)$$

where Q is the charge corresponding to the product of the current intensity and time (value measured by the equipment), R is the gas constant, T is the absolute temperature, P is the pressure and F is the Faraday constant.

It is worth noting that the $(1 - \eta)$ term corresponds only to the charge spent in parallel reactions, such as corrosion or electrolyte decomposition.

3. Results and discussion

The zwitterionic compound 3-triethylammonium−propanesultonate (TEA−PS), a white powder with a melting point of 144 °C, is prepared by the reaction of the inexpensive materials 1,3-propanesultone and triethylamine (see Scheme 1). This compound has been described as active in acid catalysed reactions, including the dimerisation of olefins [18,19].

The good performance of TEA−PS/HCl in dimerisation reactions may have resulted from the Lewis and Brönsted acid characteristics of these types of compounds, suggesting that these candidates should be evaluated in the water electrolysis process using electrolyte [18]. Using a 0.1 M solution, initial tests indicated that these compounds had poor effectiveness in water electrolysis, producing current densities with potentials of −1.7 V and −2.0 V at 678 mA cm^{-2} and 862 mA cm^{-2}, respectively.

An alternative process to improve the behaviour of TEA−PS was developed by reacting TEA−PS and HBF$_4$, as shown in Scheme 2.
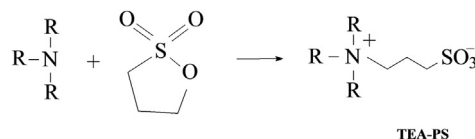
Scheme 1. Synthesis of TEA−PS precursor.
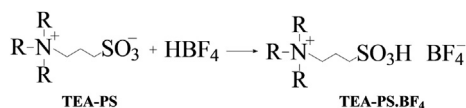
Scheme 2. Synthesis of TEA−PS·BF$_4$ IL.

The reaction takes 2 h at 90 °C, producing 3-triethylammonium−propanesulfonic acid tetrafluoroborate (TEA−PS·BF$_4$), a white viscous IL. This IL has dual characteristics of both Lewis and Brönsted acids demonstrating improved features as an electrolyte in water electrolysis.

The formation of TEA−PS·BF$_4$ can be observed using IR spectroscopy, as shown in Fig. 1.

The most important characteristics of these spectra are the O−H stretching at 3434 cm^{-1}, the C−N stretching at 1641 cm^{-1}, the C−H stretching at 2938 and the bending at both 1492 and 1397 cm^{-1}. The spectra from TEA−PS with S=O asymmetric stretching at 1224 cm^{-1} and 1187 and S−O stretching at 1037 cm^{-1} [16] are superposed in TEA−PS·BF$_4$ with the very strong B−F stretching at 1039 cm^{-1} [21,22].
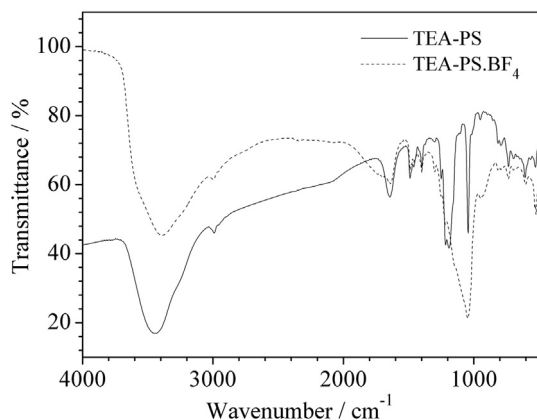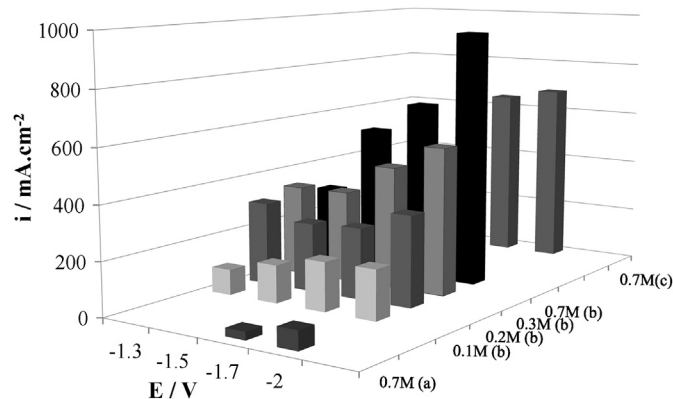
Combined with the ^{1}H NMR and ^{13}C NMR analyses discussed in the Experimental part, these results characterise the formation of TEA−PS·BF$_4$.

The use of TEA−PS·BF$_4$ as an electrolyte produced significant improvements in the performance of the electrolysis reaction, as shown in Fig. 2, which contains selected values of the current densities observed with the experimental systems and similar ones described in the literature.

These results suggest that TEA−PS·BF$_4$ significantly improves the current densities with an accompanied increase in the amount of hydrogen produced from the water electrolysis, as compared with both KOH and BMI·BF$_4$ electrolytes. At −2.0 V, the systems using BMI·BF$_4$ (0.7 M) and KOH (0.7 M) produce current densities of 80 and 583 mA cm^{-2}, respectively, with the TEA−PS·BF$_4$ (0.7 M) system producing 800 mA cm^{-2}. High efficiencies (93–99%) are observed at all concentrations, suggesting that the enhancement in the hydrogen production was significant with remarkable economic consequences. A more detailed study of the different reaction parameters has been performed.

The behaviour of TEA−PS·BF$_4$ as an electrolyte for water electrolysis is initially investigated to determine the conditions corresponding to the limiting current, as determined by the current density versus the potential curve shown in Fig. 3.

The current density increases continuously with increasing potential until −5.8 V, as shown in Fig. 3. This limit value most

Fig. 2. Effects of the potential on the current density using water electrolysis with multiple electrolytes: (a) BMI·BF$_4$, (b) TEA−PS·BF$_4$, (c) KOH. Conditions: 25 °C, working electrode surface: 0.23 cm^2.

likely results from the formation of large quantities of hydrogen that decreases the active area of the working electrode before being released. This hypothesis can be supported by the observation that the value of η (system efficiency) does not decrease for these potential values.

The effect of temperatures ranging from 25 °C to 80 °C on the performance of the system using TEA−PS·BF$_4$ at −2.0 V and −4.8 V is shown in Fig. 4.

Hydrogen production increases with increasing temperature, with Arrhenius activation energies of 9.3 kJ mol^{-1} for the 0.7 M TEA−PS·BF$_4$ solution and 12.0 kJ mol^{-1} for 0.1 M TEA−PS·BF$_4$ aqueous solutions.

A comparison of these values with those reported for other electrolytes is elucidative. For BMI·BF$_4$, a value of 23.4 kJ mol^{-1} has been reported [23]. For KOH, reports in the literature suggest activation energy values between 10.0 kJ mol^{-1} [24] and 46.0 kJ mol^{-1} [25], depending on the electrodes and the reaction conditions. With the same conditions and electrodes used in the TEA−PS·BF$_4$ experiments, an independent determination produced a value of 16.0 kJ mol^{-1} for a 0.1 M KOH solution.

For this water electrolysis process, the observed difference in the activation energies of approximately 10.0 kJ mol^{-1} between the BMI·BF$_4$ and TEA−PS·BF$_4$ electrolytes is significant. Several possible explanations may have accounted for the outstanding performance of TEA−PS·BF$_4$. Changes in the reaction path cannot

Fig. 1. IR spectra of TEA−PS (continuous line) and TEA−PS·BF$_4$ (dotted line).
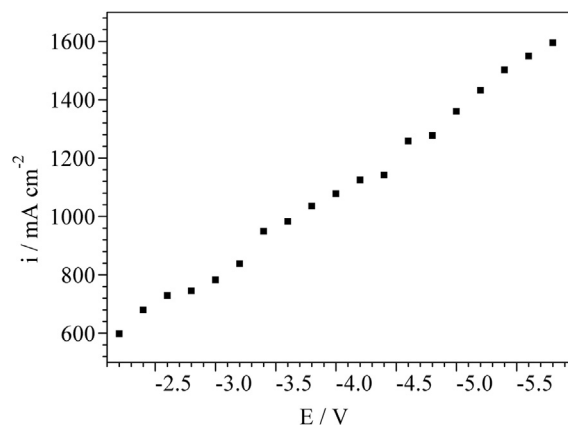
Fig. 3. Effects of the potential on the current density using water electrolysis. Reaction conditions: 25 °C, working electrode surface: 0.23 cm^2, ionic liquid concentration: 0.1 M.
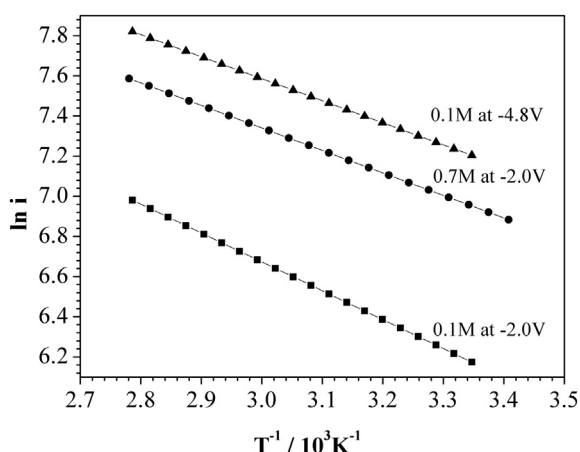
Fig. 4. Effects of temperature on the current density for the system using TEA–PS·BF$_4$ at −2.0 V and −4.8 V. Current density (i) is expressed in mA cm^{-2}.

be excluded, but no reports of these phenomena have been documented. The outstanding performance of TEA–PS·BF$_4$ may result from an enhancement of the transport of charges through this medium, with the possible formation of channels organised by the intrinsic structure of the ionic liquid and their assemblages. This transport mechanism would not be surprising, with the large number of literature descriptions of ionic liquid organisations in solution [26,27]. These possible IL structures could generate channels, allowing H$_3$O$^+$ to be easily conducted. An increased mobility of this species would then correspond with a decrease in the activation energy.

The conductivity of the solutions can be used to support this possible mechanism. The conductivity values (TEA–PS·BF$_4$ at 132.5 mS cm^{-1}, BMI·BF$_4$ at 25.8 mS cm^{-1}, KOH at 96.5 mS cm^{-1} and KCl at 52.3 mS cm^{-1}) show that TEA–PS·BF$_4$ dissociates in aqueous solutions, producing the TEA–PS$^+$ cation and the BF$_4^-$ anion. The TEA–PS$^+$ cation a Brönsted acid, ionises in water, producing the H$_3$O$^+$ ion, acidifying the solution to pH 0.8 and increasing its conductivity facilitating mass transport and the production of H$_2$. The TEA–PS$^+$ cation, a species zwitterionic, can form an organised assemblage of the IL creating channels to transport H$_3$O$^+$ ion, enhancing the conductivity values.

This structure can produce privileged transport conditions, enhancing the ionic mobility and decreasing the energy barrier involved in water electrolysis. In combination, these mechanisms could account for the observed enhancement in the hydrogen production.

Experiments comparing TEA–PS·BF$_4$ and HCl have been performed in order to demonstrate the unusual behaviour of these ILs. An example is the electrolysis of a HCl solution with pH 0.8 performed under the same experimental conditions as those employed with IL solutions. The current density obtained is 80 mA cm^{-2} that is significantly lower than the value obtained with IL solution (800 mA cm^{-2}) with the same pH.

Experiments on the transport of ions in ILs media are currently being studied in our laboratory.

4. Conclusions

A new family of ionic liquids, which are easily prepared from inexpensive reagents, can be synthesised by simple procedures in short reaction times. A representative compound of this family is 3-triethylammonium–propanesulfonic acid tetrafluoroborate (TEA–PS·BF$_4$), which is demonstrated to have outstanding electrolyte characteristics that are useful in the water electrolysis experiments.

The electrolysis experiments performed with these new electrolytes can operate at room temperatures with high efficiencies (exceeding 93%) and high current densities (i) of up to 0.96 A cm^{-2} and 1.77 A cm^{-2} at 80 °C. Comparing the TEA–PS·BF$_4$ IL with BMI·BF$_4$ IL and a commercial electrolyte (KOH), an improved current density is observed, suggesting that TEA–PS·BF$_4$ has improved characteristics in the hydrogen evolution reaction (HER) generated by water electrolysis.

The description of the outstanding performance of HER in presence of TEA–PS·BF$_4$ combined with some properties of these ILs like their very high stability and their characteristics as corrosion inhibitors enable then to be considered as potential alternatives as electrolytes for applications in industrial electrolysis systems.

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